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Rheokinetics of Linear Polymerization.

A Literature Review

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The dramatic increase of viscosity is a fundamental problem when designing a polymerization process. Since a thorough understanding of rheokinetics—the study of the coupled rheological changes and chemical kinetics in the reaction mixture—especially at high degrees of conversion, is still missing, industrial polymerization processes are often designed on basis of trial and error procedures and operate in far-from-optimal conditions. Even at laboratory scale the measurement of the viscosity of systems rapidly changing with time is troublesome and predicting quantitatively the increase of viscosity is not an easy task. The non-Newtonian character of polymeric systems makes rheokinetics an even more challenging field, and more interesting as well. In this review article the difficulties encountered by the research community, the results obtained so far and the problems still to be faced are discussed.

INTRODUCTION

When studying the kinetics of ordinary chemical reactions in the liquid phase the viscosity is not an important parameter. Both the reactants and the products are chemical compounds of low molecular weight of the same order of magnitude. Therefore, the viscosity does not depend on the degree of conversion, but only on the experimental conditions, such as the temperature of the system. Moreover, this dependence is not likely to be very significant. Thus, the viscosity remains essentially constant during the reaction and has no influence on its kinetics.

Nevertheless, for many industrially important materials the rheology, among other things the apparent viscosity, determines the ease and manner of processing of many materials. Especially for polymeric materials the rheology will be a major factor of concern. Therefore a significant part of the scientific literature on polymers is concerned with the rheology of polymeric systems and investigates the non-Newtonian

behavior of solutions of polymers in their monomers or in other solvents. Many papers and books have been published regarding the relationship between the viscosity or other rheological properties (the elastic modulus, the loss modulus, the normal stress differences) and the average molecular weight, the polydispersity and the concentration of the polymer in different flow situations.

Surprisingly, a similar attention has not been dedicated to the study of rheology *during* polymerization processes. All the same, major viscosity changes occur during the polymerization due to the formation of large, high molecular weight molecules and their subsequent entanglement. This increase in viscosity will almost certainly have an effect on the kinetics of polymerization and therewith on the final product properties. Therefore understanding the changing rheological properties and their effects during polymerization processes is a very important research area, especially in view of the not insignificant industrial applications. In fact at present polymerizations are often performed at far-from-optimal conditions, because of a lack of understanding of the relationship between rheology and kinetics (1, 2).

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A complete understanding of the kinetics of rheological changes during polymerization is still missing. This coupling between the increasing viscosity of the reacting solution and the kinetics of the polymerization process is a relatively new field of research and has been called rheokinetics. The aim of this paper is to review the most recent results that have appeared in the scientific literature, trying in the process to spread some light on this still open and fascinating problem.

We shall confine our discussion to the rheokinetics of linear polymerization. Those interested in the rheokinetics of curing systems that form three-dimensional molecular networks should refer to a review article (3) or to a recently published book (4) concerning this subject.

AN OVERVIEW OF EXPERIMENTAL METHODS USED

A rheokinetic study of polymerization requires reliable measurements of the viscosity. Since the viscosity may increase by as much as 6–7 orders of magnitude in a relatively short time, it is very difficult, if not impossible, to cover the whole polymerization process with a single experiment.

The Ubbelohde viscometer and the Couette rheometer have mostly been used to investigate the early stages of the polymerization. The former measures the viscosity close to a zero-shear situation, the latter in shear flow.

The later stages of the polymerization are better studied with a cone and plate rheometer. This geometry induces a uniform shear rate in the whole sample and is therefore ideal to investigate the influence of shear rate on the viscosity increase and on the kinetics of a polymerization (5).

When using the Couette or the cone and plate rheometer the rotational velocity of the rotating element is an important parameter. Some authors (6–8) have performed experiments with the Couette geometry decreasing the shear rate during the polymerization in order to obtain viscosity measurement over a wide range of values. A high shear rate is initially required to have a measurable torque and a low shear rate is required later to avoid too high a torque that would damage the torque sensor. This procedure is, of course, rather tricky and valid only in the initial stage of the polymerization, where the sample can be considered to be Newtonian. Moreover the high rotational velocity required at very low viscosity might induce secondary flows in the gap between the two cylinders, affecting the reliability of the measurement.

Although the measurement of the viscosity is the main feature of a rheokinetic study, a parallel analysis of the increase of the conversion during the polymerization is useful to confirm and/or refine the rheokinetic results. Also further insight would be gained by a simultaneous measurement of the evolution of the average molecular weight and polydispersity of the polymerizing sample.

Unfortunately, experimental equipment capable of measuring the viscosity, the conversion and the molecular weight (or even only two of these three parameters) at the same time is not available on the market. Modified versions of the Ubbelohde rheometer (9, 10) can measure the viscosity and, at the same time, the conversion with a dilatometric technique, but they work in the absence of shear and can be used only in the early stage of the polymerization.

So, in general, the viscosity, the conversion and the molecular weight must be necessarily measured in different pieces of equipment, and thus in different flow and, probably, different thermal conditions. Therefore the results obtained in parallel with different experimental pieces of equipment must be compared carefully.

The conversion is often measured in quiescent conditions by a calorimetric or spectrometric technique, whereas the viscosity is measured in shear flow. Therefore the data can be compared properly only in the initial stages of the polymerization where Newtonian behavior can be assumed. In later stages, the comparison is valid only under the assumption, to be verified (see the discussion of this issue later in this paper), that the shear rate has no influence on the kinetics of the polymerization.

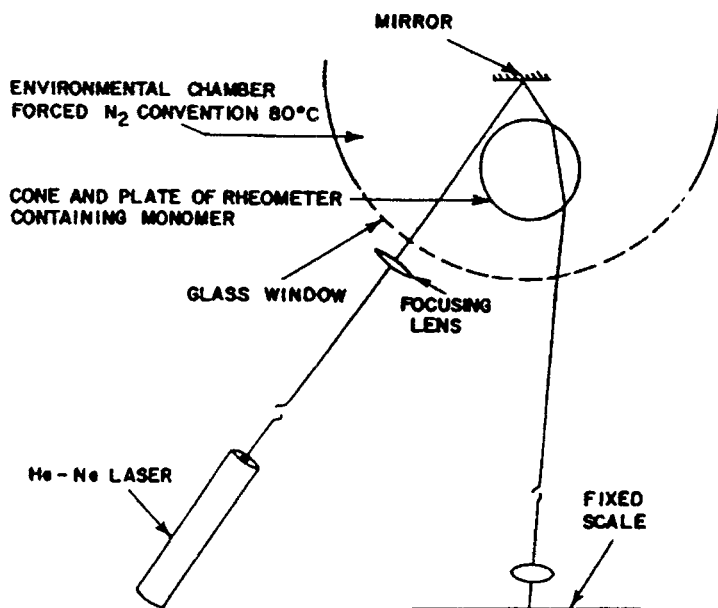
An alternative approach is to perform the polymerization in the rheometer several times, stop the polymerization after different reaction times by thermal quenching and/or adding an inhibitor and store the samples for conversion analysis. However the conversion versus time curves obtained in this way will be troubled by the inherent poor reproducibility of initial lag times of polymerization processes. Furthermore, polymerizations usually being fast processes, the poor reproducibility of the manual operations required to remove and quench the sample may cause further errors. Finally, removing a highly viscous sample from the cone and plate rheometer may be troublesome and induce damages to the surfaces of the cone and of the plate that must remain smooth and free of grooves.

In order to overcome these problems, several authors have tried to develop self-made rheometers that allow simultaneous measurement of viscosity and conversion.

Malkin (11), for example, studied the rheokinetics of the anionic polymerization of dodecalactam with a reactor vessel provided with a thermocouple and a transducer of an ultrasonic viscometer under near adiabatic conditions. The temperature increase due to the heat released during the polymerization was used as a measure of the degree of conversion.

Kale and O'Driscoll (12) studied the rheokinetics of the free radical polymerization of *n*-laurylmethacrylate (*n*-LMA) with a modified rheometer. This rheometer was of the cone and plate type and also allowed determination of the conversion by measuring the change in diffraction of a laser beam shone through the polymerizing sample (Fig. 1).

Fig. 1. A schematic representation of the modified cone and plate rheometer used by Kale and O'Driscoll (12) to measure the viscosity and the conversion simultaneously during the polymerization of *n*-laurylmethacrylate. A laser beam is shone through the sample and the change in the refractive index is monitored on a fixed scale, which gives a measurement of the viscosity.



Biesenberger *et al.* (13) tried to modify a Couette rheometer and provided it with a calorimetric cell for differential scanning calorimetry (DSC). This would allow measuring the viscosity and the conversion increase during polymerization simultaneously. Unfortunately the many technological problems encountered could not be overcome completely, as these authors themselves admitted. Moreover the very complicated structure of this rheocalorimeter caused cleaning problems when performing experiments with real polymeric systems and not with model fluids for testing purposes.

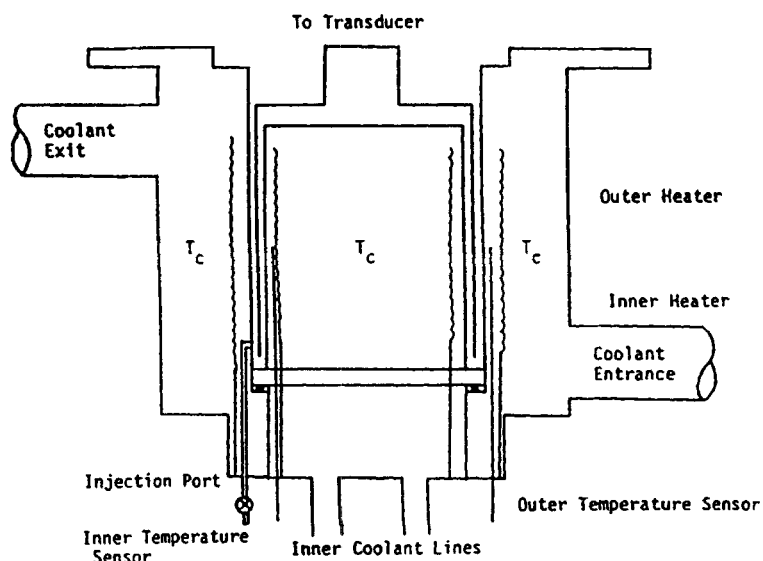
Rosendale and Biesenberger (14) had more success a few years later. They modified a Couette rheometer with a very narrow gap to facilitate temperature control

of the polymerizing sample (Fig. 2). A temperature sink was provided by a cooling liquid circulating around the annulus at approximately 20°C below the reaction temperature. The rate of reaction was determined measuring the power output of the heaters that maintained the reaction temperature. As long as the polymerization produced heat, the heaters decreased their power output.

Other authors preferred to perform rheokinetic studies with completely different techniques. Meissner and Poltersdorf (15), for example, used not only a "classical" Couette rheometer but also laboratory processing machines as a midget kneader or a laboratory extruder.

Finally, Malkin *et al.* (16) followed an alternative and original approach to rheokinetics. They exploited the

Fig. 2. The rheocalorimeter used by Rosendale and Biesenberger (14). It combines Couette rheometry with dynamic scanning calorimetry.



so-called 'Toms' effect to study the very early stages of a polymerization process. The Toms effect consists of the increase in pumpability of a fluid caused by the addition to the fluid of small amounts of a polymer. This reduces the turbulence, and therewith the friction in pipelines. The literature concerning the Toms effect is reviewed elsewhere (17, 18).

These authors performed the polymerization of 1-hexene with a Ziegler-Natta catalyst and took samples of the polymerizing mass at fixed times. The samples were then diluted with heptane and transferred to a handmade capillary "turbulent" rheometer. The diluted samples were forced to flow in the capillary rheometer and the friction factor λ was determined according to

$$\lambda = \frac{D}{4L} \frac{\Delta P}{\frac{1}{2} \rho v^2} \quad (1)$$

where D is the diameter, L is the length of the capillary, ΔP is the applied pressure across the capillary, ρ is the density and v is the average velocity. The latter was determined measuring the amount of liquid collected at the end of the capillary in a certain time. The Toms effect was expressed by the value of the drag reduction, DR , defined according to:

$$DR = \frac{\lambda_0 - \lambda(t)}{\lambda_0} 100\% \quad (2)$$

where λ_0 is related to the time zero of the polymerization and $\lambda(t)$ is the value of the friction factor of the diluted sample after a certain reaction time t .

The drag reduction, and thus the Toms effect, increases as the polymerization goes on. Concentration versus time profiles could be calculated beginning from the very early stages of the polymerization with the help of a calibration curve of the drag reduction that was defined dissolving known amounts of a polymer in the solvent.

RHEOKINETICS OF POLYMERIZATION

a) Low Conversion. Newtonian Behavior

In this section we discuss data referring to low degrees of conversion and/or to polymerization performed in solution. For this reason the authors of the articles reviewed in this section could assume, sometimes implicitly, that the polymerizing fluid was Newtonian.

The term "rheokinetics" appeared for the first time in the scientific literature in 1980. Biesenberger and Gogos (19) recognized the importance of modeling the viscosity increase during the polymerization process as a function of experimental conditions (shear rate, temperature), average molecular weight and conversion in order to make reactive polymer processing more profitable. They also acknowledged the almost complete lack of useful literature data.

Malkin (11) wrote one of the classic papers on rheokinetics. In this paper, he defined rheokinetics as the rheology of systems changing with time because of

ongoing polymerization that cannot be studied without taking into account the kinetics of the chemical reactions.

The underlying idea of this paper (and of much of the literature regarding rheokinetics) is that the rheological behavior of a reacting polymer system at a certain time and of a nonreacting system having the same concentration of polymer and the same average molecular weight are the same.

The viscosity η was considered to be a power law function of the number-averaged degree of polymerization N and of the concentration of the polymer ϕ .

$$\eta = KN^a \phi^b \quad (3)$$

where K , a and b are constant

This relationship was the starting point for deriving a rheokinetic model, i.e. a relationship for the viscosity increase during polymerization as a function of time or conversion β . In fact, with the help of models for the chemical kinetics, N and ϕ can be expressed as a function of β and β as a function of time t .

The derivation of the rheokinetic model is different for different kind of polymerizations and will be explained in the following of the paper. For the time being it will suffice to say that the rheokinetic models derived in (11) consisted of power law relationships. Experimental data confirmed this trend, and the power law exponents of the rheokinetic experiments were in agreement with the ones obtained performing a rheological study of nonreacting polymer solutions in their own monomer. They also validated the assumption that the rheological behavior of a reacting system is equivalent to the one of nonreacting polymer solutions.

Moreover, performing the rheokinetic experiments—i.e. measuring the viscosity increase with time—at different temperatures it was possible to obtain Arrhenius plots and to derive the apparent activation energy of the polymerization process.

In the subsequent years a few papers were published following Malkin's footsteps.

Malkin *et al.* (10) studied in detail the rheokinetics of free radical polymerization, particularly in the early stages. For free radical polymerization the concentration of polymer ϕ is equal to the degree of conversion of the monomer:

$$\phi = \beta = \frac{[M]_0 - [M]}{[M]_0} \quad (4)$$

where $[M]_0$ and $[M]$ are the initial and the current concentration of the monomer.

Moreover the following two relationship holds if chain transfer reactions are not considered:

$$N = \frac{[M]_0 \beta}{[I]_0 (1 - e^{-k_t t})} \quad (5)$$

$$\ln(1 - \beta) = \frac{2f^{1/2}k_p}{k_t^{1/2}k_i^{1/2}} [I]_0^{1/2} (1 - e^{-k_t t}) \quad (6)$$

where $[I_0]$ is the initial concentration of the initiator, f is the initiator efficiency, t is the time and k_i , k_p and k_t are the rate constants of the initiation propagation and termination reaction (10).

Substituting Eqs 4 and 5 into Eq 3, Malkin *et al.* derived a rheokinetic model for the dependence of the viscosity on the degree of conversion.

$$\eta = K\beta^b \left(\frac{[M]_0\beta}{[I]_0(1 - e^{-k_i t})} \right) \quad (7)$$

Further substitution of (6) yielded the relationship between viscosity and time.

$$\eta = K[M_0]^a[I_0]^{-a} \left[1 - \exp\left(-\frac{2f^{1/2}k_p}{k_i^{1/2}k_t^{1/2}}[I_0]^{1/2}(1 - e^{-k_i t})\right) \right]^{(a+b)} \quad (8)$$

Equations 7 and 8 make it possible, according to (10), to give a complete description of the change in the viscosity of reacting media during free radical polymerization if the kinetic constants are known. This is only partially true because the influence of the shear rate on the viscosity is not taken into account by Malkin and co-authors. Another problem lies in the fact that the kinetic constant of the propagation reaction may change during the polymerization because of self-acceleration of the rate of polymerization (Trommsdorff or gel effect).

However, the authors confined their analysis to low degrees of conversion. In this way, the kinetic constant could be assumed to be invariable, and Eqs 5 and 6 could be simplified expanding them into power series until the linear terms.

Substituting Eq 4 and the linearized forms of Eqs 5 and 6 into Eq 1, the following simple relationships were obtained:

$$\eta = A_1[I]_0^{-(1/2)a}\beta^b \quad (9)$$

$$\eta = A_2[I]_0^{(1/2)(b-a)}t^b \quad (10)$$

A_1 and A_2 are proportionality factors containing the kinetic constants of the initiation, propagation and termination reaction. The viscosity is proportional to $[I]_0^{-a/2}$ when the degree of conversion and all the other experimental conditions are kept constant and to $[I]_0^{(b-a)/2}$ when the reaction time and all the other experimental conditions are kept constant.

In (10) the bulk polymerization of a few methacrylates and of styrene was investigated with an Ubbelohde rheometer. Comparing experiments performed at different initiator concentration, but otherwise the same experimental conditions, made it possible to calculate the power law exponents a and b . They agreed once again with the ones obtained from viscometry of non reactive polymer solutions.

Some experiments were also performed for the solution free radical polymerization of methylmethacrylate, using cyclohexane as a precipitant and toluene as a solvent. A very peculiar behavior was obtained.

The viscosity increased initially, then decreased and finally increased again after reaching a local minimum (Fig. 3). This was attributed to precipitation of the polymer, which begins exactly when the viscosity starts to decrease, and could be observed to cause turbidity of the system. Rheokinetic experiments can thus give useful information about changes of the system physical state.

Bulai *et al.* (20) used viscosity measurements for a better understanding of the kinetics of a polycondensation process, where the relationship between the overall rate of the process and the rate of elementary reactions is not straightforward as in free radical polymerization. NMR spectroscopy was used to follow the rate of formation or consumption of seven chemical species (among which the two monomers), while viscosity changes were studied with a Couette rheometer to investigate the 'macrokinetics' of the whole process.

The authors defined the degree of conversion as follows:

$$\beta = \frac{x_0 - x}{x_0} \quad (11)$$

where x_0 and x are the initial and current concentration of a reactive group.

They also stated that for polycondensation processes the number-averaged degree of polymerization can be expressed as:

$$N = (1 - \beta)^{-1} \quad (12)$$

They considered polycondensation processes of bi-functional compounds that are not complicated by diffusion limitation. The kinetics of such a reaction was described by an equation of second order.

$$\frac{dx}{dt} = -kx^2 \quad (13)$$

where k is a kinetic constant.

Integrating Eq 13 with the assumption that $x_0 kt \gg 1$ and substituting in Eq 12, the following expression for N was obtained:

$$N = x_0 kt \quad (14)$$

In the case of polycondensation Bulai *et al.* found that the following relationship holds between the viscosity and the degree of polycondensation:

$$\eta = KN^a \quad (15)$$

They substituted Eq 14 in Eq 15 and obtained the following rheokinetic equation:

$$\eta = K(x_0 kt)^a \quad (16)$$

Therefore also for polycondensation the rheokinetic model consists of a power law relationship. According to the theory of rheology of nonreacting polymer solutions, the exponent a is equal to 1 until a critical molecular weight is reached. Afterwards it is equal to 3.4.

In order to test the validity of the rheokinetic model (16) Bulai *et al.* polymerized polyarylsulfoxide by

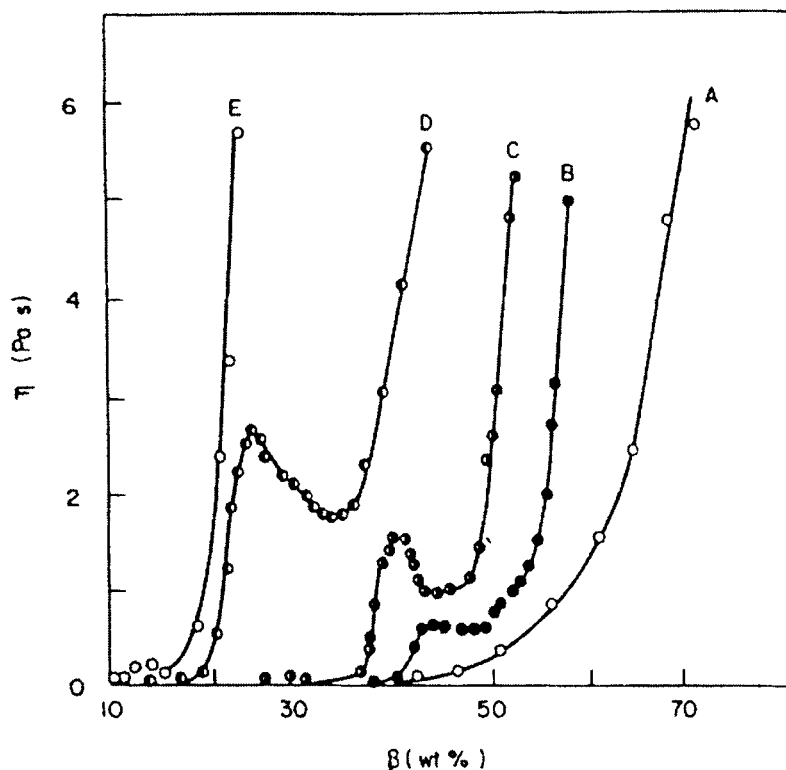


Fig. 3. The viscosity vs. degree of conversion during the polymerization of methyl methacrylate in the presence of a cyclohexane and toluene (10). A local minimum in the curves is due to the precipitation of the polymer. Different curves refer to different initial mixture compositions. Mixture composition, methylmethacrylate: cyclohexane: toluene (wt%) respectively: curve A, 50:15:35; B, 50:30:20, C, 50:32.5:17.5; D, 50:37.5:12.5; E, 50:37.5:12.5.

mixing equimolar solutions of dichlorodiphenylsulfone and the sodium salt of diphenilolpropane in both a Couette and a cone and plate rheometer.

Viscosity measurements confirmed the value of 3.4 after a short initial reaction time. The change with time of the number average degree of polycondensation was in agreement with the assumed second-order kinetics. Experiments performed at different temperature made it possible to determine the value of the apparent activation energy. The value obtained was in agreement with literature data. When the dichlorodiphenylsulfone content was decreased, the viscosity increase brought about a deceleration of the process because the reaction passed into the diffusion-controlled stage. This was confirmed by a reduction of the reaction rate constants derived by NMR spectrometry.

Another rheokinetic study was performed by Kulichikhin *et al.* (6) and Polushkina *et al.* (7). They studied in detail the influence of initiator and monomer concentration on the increase of viscosity during the free radical polymerization of acrylamide in aqueous solution. Different experiments performed at the same monomer concentration and at different initiator concentration showed (Fig. 4) that increasing the initiator concentration, the time required to complete the reaction decreased, as well as the final value of the viscosity. Since the higher the initiator concentration, the lower the average molecular weight of the polymer obtained, it can be concluded that the rheokinetic analysis confirmed the general theory of free radical polymerization (21). In fact, it is known that a low initiator

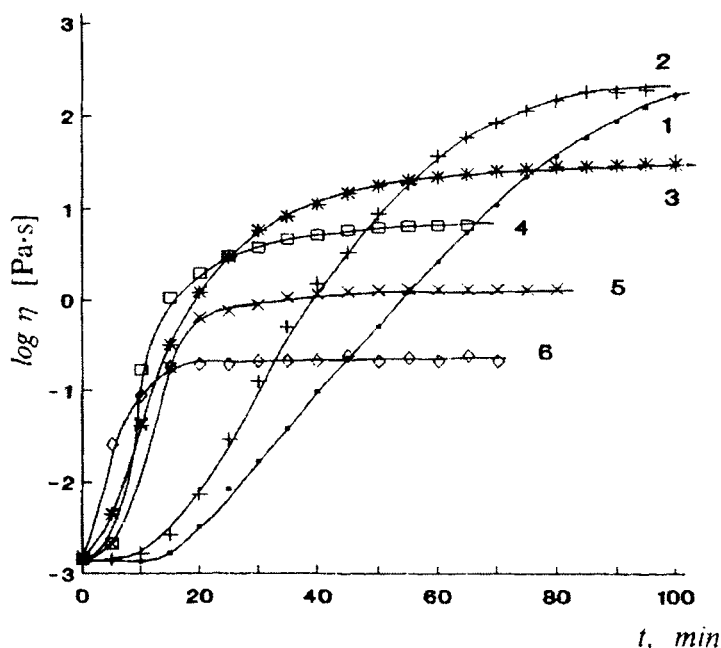
concentration is required to have high molecular weight polymers, but this results in longer reaction times.

Polushkina *et al.* (8) made a further step in the rheokinetic analysis by defining and, for one particular case, solving the 'direct' and the 'inverse' rheokinetic problem. The direct rheokinetic problem consists in predicting the viscosity increase during the polymerization with the help of a kinetic model. The inverse rheokinetic problem consists in determining the kinetic parameters on the basis of rheokinetic measurements of the viscosity during the polymerization. The direct problem was solved in the initial stage of a free radical polymerization characterized by a second order initiation reaction. The rheokinetic equations $\eta(\beta)$ and $\eta(t)$ were derived as in (10), but they are slightly different because the initiation reaction considered in (8) was of the second order and not of the first as in (10) and they are not reported here. The inverse rheokinetic problem was solved deriving the $\beta(t)$ relationship from the experimental dependence $\eta(t)$. The derived $\beta(t)$ relationship was linear and from its slope it was possible to determine that $k_p/k_t^{1/2} = 3.4$. This value falls within the interval 3.0–4.7 reported in the literature for the polymerization studied in (8).

b) Intermediate and High Conversions. Non-Newtonian Behavior

A few papers have also been published concentrating on the latest stages of polymerization, where the hypothesis of Newtonian behavior is no longer valid.

Fig. 4. The increase of viscosity during the acrylamide polymerization in water solutions (6). Different curves refer to different initiator concentration: 0.1 wt% for curve 1, 0.2 for curve 2, 0.5 for curve 3, 0.7 for curve 4, 1.0 for curve 5 and 5.0 for curve 6. A lower initiator concentration results in longer reaction times, but higher plateau values of the viscosity.



Kale and O'Driscoll (12) studied the rheokinetics of the free radical polymerization of *n*-laurylmethacrylate (*n*-LMA) with a modified cone and plate rheometer in oscillatory mode. The viscosity and conversion data showed the absence of the gel or Trommsdorff effect, in agreement with the literature concerning their reaction. The viscosity increased with the conversion according to a power law trend, in agreement with (11). The storage modulus G' and the loss modulus G'' both increased with the reaction time. Initially $G'' > G'$ but at certain critical conversion an inversion occurred, indicating the presence of entangled polymer coils.

Yemelyanov *et al.* (9) studied the rheokinetics of free radical polymerization of many vinyl monomers using two different rheometers, one for low and one for high conversions. They confirmed that there is a power law relationship between viscosity and conversion. The power law exponent, though, is not constant throughout the polymerization. It is equal to 1, 4 to 6 and 10 to 25 at low, intermediate and high conversions, respectively (Fig. 5). The exact values depend on the vinyl monomer and on the experimental conditions. These three regions correspond to Newtonian fluid, non-Newtonian fluid and high elastic rubbery state. The transition from the second to the third region coincides with the onset of self-acceleration of the polymerization. According to the authors, a fourth region is also present at the very end of the polymerization where the systems are in the glassy state, but no viscosity data are presented to prove it, probably because steady shear measurement of glassy materials resulted in irregular and irreproducible viscosity trends.

Rosendale and Biesenberger (14) followed the approach of Malkin (10) with some modification to develop a rheokinetic model for free radical polymerization

similar to Eqs 9 and 10, but one that incorporates the possibility of self-acceleration and therefore can also be applied at later stages of the polymerization. Moreover, they dropped the assumption made in (10) that the degree of polymerization remains constant throughout free radical polymerization. They also used a rheocalorimeter to measure simultaneously the increase of conversion and viscosity (in oscillatory mode) during two different free radical polymerizations. The experimental results agreed with the rheokinetic model. Particularly, a peak in the heat released during the polymerization was obtained simultaneously with an exponential growth of the viscosity, denoting the onset of self-acceleration. Also the polycondensation of a linear polyurethane was studied but in this case the rheocalorimeter failed to give useful results. In fact, polycondensation reactions usually have huge viscosity effects but negligible thermal effects and therefore measurement of conversion with a calorimetric method was troublesome in this case.

The above-mentioned three research teams, Kale and O'Driscoll (12), Yemelyanov *et al.* (9) and Rosendale and Biesenberger (14) performed their experiments at a fixed shear rate and did not investigate the influence of the shear rate on rheokinetics. However, the shear rate is an important parameter in rheokinetic investigation at intermediate and high degrees of conversion because the reacting fluid is likely to be non-Newtonian, especially when no solvents are used.

A first attempt to study this problem was made by Malkin and Kulichikhin (22), who studied the anionic polymerization of caprolactam. They measured the increase of viscosity during the polymerization at different shear rates and concluded that the rate of polymerization is slowed down by a higher shear rate.

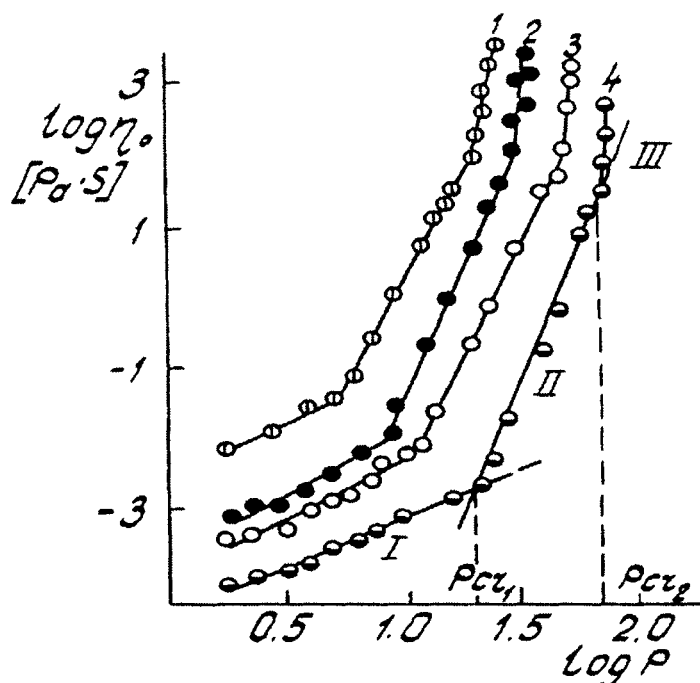


Fig. 5. The increase of viscosity during the polymerization of vinyl pyrrolidone (curve 1) and octyl methacrylate (curves 2-4) (9). Three different power law regions can be distinguished.

Cioffi *et al.* focused their attention on the later stages of the bulk free radical polymerization of styrene and *n*-butylmethacrylate (5). They showed with a cone and plate rheometer that the isothermal increase of viscosity during the polymerization can be fitted by a double power law trend and they considered the difference of the two power law exponents to be a measure of the self-acceleration (Trommsdorff or gel effect). Comparing the power law exponents obtained at different shear rate, but otherwise the same experimental conditions, it was demonstrated that the self-acceleration (Trommsdorff or gel effect) is less pronounced when the polymerization is performed at a high shear rate (Fig. 6). At values of about 200 s^{-1} the self-acceleration

is greatly reduced, if not eliminated. Since the self-acceleration is due to a decrease of the termination rate constant (21, 23), the latter must be considered a function not only of conversion but also of shear rate.

c) Alternative Approaches to Rheokinetics

The rheokinetic models discussed so far are based on rheological and kinetic relationships between viscosity, molecular weight, conversion, and kinetic constants. A complete alternative approach was attempted by Meissner and Poltersdorf (15).

They acknowledged the validity of Malkin's approach based on the chemistry of the polymerization but preferred to follow a different route that they considered

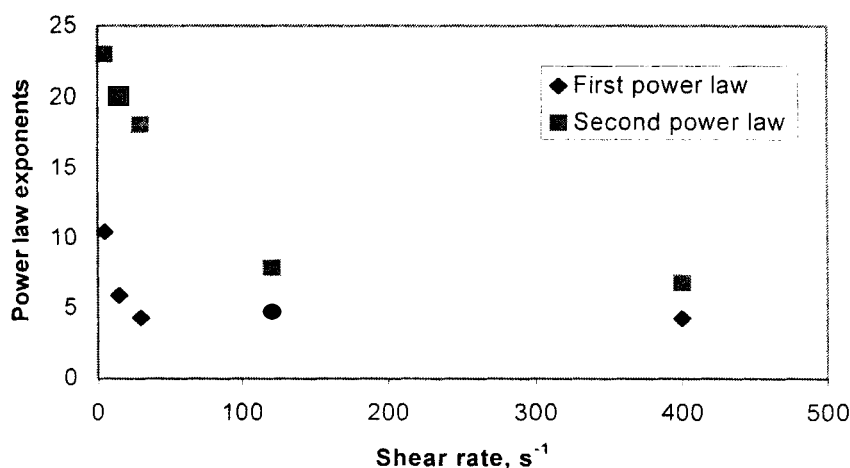


Fig. 6. The power law exponents obtained from the curves of the viscosity increase as a function of shear rate for the polymerization of styrene at 90°C (5).

more valid for possible application of rheokinetics to reactive processing of polymers involving complex reactions. Meissner and Poltersdorf assumed that the viscosity changes are due to competing destruction and structurization processes. They both consist of complex reactions of unknown order. Structurization processes lead to the formation of the polymer molecules, while the destruction processes cause their decomposition and can be of chemical, thermal or mechanical origin.

A rheokinetic model of the viscosity change during polymerization was derived which consists in a very complicated differential equation containing 11 parameters. These parameters are mainly the kinetic constants and the exponents describing the reaction orders of the structurization and destruction processes.

A Couette rheometer and laboratory processing machines (midget kneader, laboratory extruder) were used to study the effect of small and high thermomechanical loads on the rheological properties at small and high mechanical loads, respectively. The model parameters were determined by fitting experimental results to the model. Although this approach is quite interesting and directly oriented towards practical applications, its major limitation is that the number of parameters is too high to give clear-cut indications about the validity of the model and the reliability of the values of the parameters. Moreover, the physical meaning of some of the parameters is not clear.

Other authors used rheokinetic arguments to model the behavior of tubular reactors aiming at the use of continuous reactors for the production of polymers. Malkin *et al.* (24) pointed out that the velocity profile inside a tubular reactor differs considerably from the Poiseuille profile as a consequence of the rheokinetic effect, i.e. the ongoing polymerization in the tube and the consequent increase of viscosity. They developed a mathematical model to determine the average molecular weight and the polydispersity inside a tubular reactor at different degrees of conversion for the isothermal polymerization of dodecalactam, whose enthalpy of polymerization is practically equal to zero. Solving the equations they discovered that even for this isothermal polymerization the deviation of the real velocity profile from the Poiseuille profile has a great influence on the average molecular weight and on the molecular weight distribution.

Baillagou and Song made a further step and used successfully a rheokinetic approach to model the pre-polymerization of methylmethacrylate in tubular reactors below (25) and above (26) the glass-transition temperature. They combined mass and heat balances for the tubular reactor with constitutive equations for the viscosity and performed experiments that confirmed the validity of their model. Higher temperatures avoided sedimentation of glassy polymer in the tubes but resulted in a lower molecular weight of the product.

An alternative and original approach to rheokinetics was also followed by Malkin *et al.* (16), who exploited

the Toms effect to study the very early stages of a polymerization process, as explained previously. The polymer formation was noticeable even 30 seconds after the start of the polymerization when the polymer concentration in the reactive mass was only 15 ppm. At this early stage other widely used techniques to follow polymerization kinetics (dilatometric, calorimetric, spectral, chromatographic) or rheokinetics are not sensitive enough. The advantage of being able to follow the very early stages of the polymerization lies in the fact that they reflect to the inherent activity of the catalyst. This method therefore makes it possible to compare different catalysts.

The method is valid for polymerizations that proceed at a constant average molecular weight. In this case the variation of the drag reduction is due only to the change in concentration of polymer. If the molecular weight and the concentration of polymer both change, the drag coefficient increases also as a consequence of the increase of average molecular weight and it is difficult to separate the two contributions to the drag reduction. Therefore, in this case it is not possible to define a reliable relationship between the conversion and the drag coefficient.

In principle, the Toms effect can be used also to follow the later stages of polymerization, simply diluting the samples, but it should be remembered that very high dilution ratios induce experimental errors.

CONCLUSIONS

A good knowledge of the increase of the viscosity during a polymerization process is fundamental for the optimal design of polymerization reactors and of processes where the polymer is produced directly in the desired shape (reactive extrusion, reactive injection molding). Solvents are often used to minimize the viscosity increase, and all the technological difficulties that it brings about, but they are neither cheap nor environmentally friendly. Moreover, they cause an increase in the energy required and their use means that an extra separation step is required at some point of the production process.

Therefore a rheokinetic study of polymerizations is necessary to design improved and more profitable polymerization processes.

Surprisingly, the scientific literature concerning rheokinetics is not abundant, probably because the rheological studies of reacting fluids is not straightforward with the rheometers currently available on the market, which are designed mainly for nonreacting materials.

So far most authors have concentrated on the early stages of the polymerization and on solution polymerization. In fact, in both cases the reacting fluid can be assumed as Newtonian, which simplifies greatly the experiments themselves, the interpretation of experimental data and the modeling of the viscosity increase. A result common to all the papers examined was the power law trend of the increase in viscosity, after an

initial lag time. The possibility of predicting the increase of the viscosity and of determining kinetic parameters from rheokinetic experiments are significant results.

At high degrees of conversion, non-Newtonian behavior sets in, which complicates the rheokinetics greatly and, at the same time, makes the rheokinetic results much more valuable with a view to possible industrial application. The possibility of self-acceleration and the search for conditions to reduce it are a complicating factor and, at the same time, an important challenge.

Notwithstanding the remarkable result that the gel effect can be reduced by high shear rates, many questions remain open. Particularly, reliable expressions for the increase of viscosity incorporating the dependence on the shear rate are yet to be derived.

Moreover the erratic and complicated fluidodynamic conditions in industrial reactors as batch reactors or extruders are very different from the ones taking place in laboratory rheometers, which are clearly defined and easy to control and reproduce. This opens the door to another challenging and fascinating problem still to be faced: the scale-up of laboratory rheokinetic studies.

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